

Anderson, Mr. Lawrence Rissman, and Mr. Michael Vary for help with this work.

## References and Notes

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## Overlap and the Prevalence of Banana Bonds in Free Radicals and Carbenes

Sir:

Evidence suggesting bent bonds (lack of orbital following) from the central carbon of numerous organic free radicals and carbenes is scattered through the literature,<sup>1-12</sup> but no one has discussed the generality of this phenomenon or its source. We were surprised to find that this bond bending can be understood semiquantitatively in terms of maximization of orbital overlap. We now believe that substantial distortion should be expected whenever the symmetry of a radical or carbene permits.

Table I presents the 13 relevant examples known to us of hydrocarbon free radicals and carbenes where internuclear

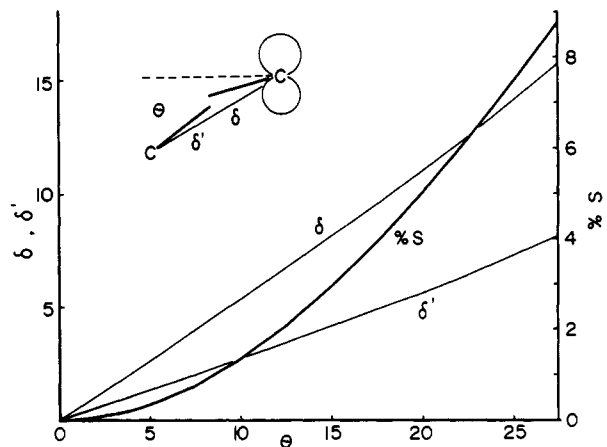


Figure 1. Orbital following in the *tert*-butyl radical calculated by maximization of overlap.

angles and hybridization angles at the functional carbon have been measured, calculated, or estimated. To compare systems with twofold and threefold rotational symmetry, angles from the plane normal to the symmetry axis are reported (see Figure 1 of ref 3) rather than angles among nuclei or between atomic hybrids. In every case but one the bonding hybrids of the central carbon fall short of pointing toward the nuclei to which they bind, and by as much as 16°. Distortion in the *tert*-butyl and vinyl radicals and in methylene (and perhaps in diphenylmethylene) is especially striking, because ring strain could not be responsible for bond bending in these acyclic molecules. The methyl radical, which must have straight bonds in its planar, minimum-energy geometry, shows substantial bond bending as it undergoes out-of-plane distortion.

From the valence-bond viewpoint we say a carbon atom adjusts its hybridization to minimize the molecular energy according to two considerations: (a) it must hold down the valence state promotion energy by maximizing the fraction of the 2s atomic orbital in the occupied hybrids; and (b) it must maximize the strength of the bonds to be formed.<sup>13,14</sup> Although the first consideration is very important with the three valence electrons of a carbocation or the five of a carbanion, it is of little importance when four valence electrons are distributed one to each of the four orthogonal hybrids.<sup>15</sup> For radicals and carbenes valence state promotion energy should be significant only when the bonds are strongly polar.<sup>14</sup> In these species, as in tetravalent carbon, bond strengths dominate hybridization.

Since the earliest discussions of hybridization, orbital overlap has been invoked as a criterion of bond strength.<sup>21</sup> Recently Randić and his collaborators have used overlap maximization at fixed nuclear geometries to determine atomic hybridization in strained-ring hydrocarbons.<sup>20</sup> These hybrids are similar to those resulting from transformations which localize molecular orbitals calculated by *ab initio* or semiempirical methods, and they correlate even better than the latter with values measured empirically by such criteria as <sup>13</sup>C-H coupling constants.<sup>22</sup>

The ability of an atomic hybrid to overlap depends both on its direction and on its extension. Although it has repeatedly been asserted that sp<sup>3</sup> hybrids give the best overlap,<sup>23</sup> Coulson showed that at normal C-C bonding distances overlap maximized near sp hybridization.<sup>13</sup> In a free radical where one of the central carbon's atomic orbitals is singly occupied and not involved in bonding, the other three hybrids are free to appropriate some or all of its s character. Up to some limit overlap may increase if the greater extension of the bonding hybrids more than compensates for their departure from the internuclear axes. Thus the bonds may bend to maximize overlap.<sup>24</sup>

The  $\delta_{\text{calcd}}$  column of Table I reports the amount of bond

Table I. Bond Bending in Free Radicals and Carbenes

Species	$\theta$	$\theta'$ <sup>a</sup>	$\delta$	$\delta_{\text{calcd}}$ <sup>b</sup>	% 2s <sup>b</sup>	Ref
Methyl <sup>a</sup>	5 <sup>c</sup>	3–4 <sup>d,e</sup>	1–2	2	0.6	1
	20 <sup>c</sup>	11–16 <sup>d,e</sup>	4–9	9	8	1
<i>tert</i> -Butyl	19 <sup>d</sup>	14 <sup>e,f</sup>	5	10	4	2
1-Triptycyl	23 <sup>g</sup>	12 <sup>e</sup>	11	11	8	3
Phenyl	30 <sup>g</sup>	22 <sup>d</sup>	8	11	11	4
2,4,6-Tri- <i>tert</i> -butylphenyl	30 <sup>g</sup>	19 <sup>e</sup>	11			5
Polycarboxyphenyls	30 <sup>g</sup>	21 <sup>e</sup>	9			6
Vinyl <sup>h</sup>	25 <sup>d</sup>	15 <sup>e</sup>	10	6, 9	10	1e, 7
Methylene	22 <sup>d</sup>	17 <sup>e,i</sup>	5	5	10	8
Diphenylmethylene <sup>k</sup>	20 <sup>j</sup>	$\geq 13$ <sup>e</sup>	$\leq 7$			9
Diphenylmethylene <sup>l</sup>	16 <sup>j</sup>	18 <sup>e</sup>	–2			10
Fluorenylidene	27 <sup>g,j</sup>	21 <sup>e,i</sup>	16	13	16	11, 12
Cyclopentadienylenide	37 <sup>g</sup>	22 <sup>i</sup>	15			12
Indenylenide	37 <sup>g</sup>	22 <sup>i</sup>	15			12

<sup>a</sup> Angle of bonding hybrid from the plane normal to the symmetry axis ( $\delta = \theta - \theta'$ ). <sup>b</sup> From maximization of overlap. <sup>c</sup> Methyl is planar in its lowest energy geometry; its zero-point rms vibrational amplitude is 5°. <sup>d</sup> From MO or VB calculation. <sup>e</sup> From <sup>13</sup>C hfs analysis. <sup>f</sup> From H hfs analysis. <sup>g</sup> From related hydrocarbon. <sup>h</sup> Since vinyl lacks a symmetry axis,  $\theta$  and  $\theta'$  relate to internuclear and interorbital angles;  $\delta_{\text{calcd}}$  angles are between the radical hybrid and the hybrids which bind H and C, respectively. <sup>i</sup> From zero-field splitting analysis. <sup>j</sup> From proton ENDOR. <sup>k</sup> Solid solution in benzophenone. <sup>l</sup> Solid solution in 1,1-diphenylethylene.

bending predicted by overlap maximization.<sup>25</sup> Agreement with the “experimental” values of  $\delta$  is striking.<sup>26</sup> Figure 1 presents the results of optimizing the C–C overlap in *tert*-butyl radical for various amounts of out-of-plane distortion, assuming sp<sup>3</sup> hybridization of the methyl carbons. Here  $\delta$  is about half  $\theta$ , and  $\delta'$  about half  $\delta$ .

The prevalence of bent bonds in radicals and carbenes has several implications for structural work. Obviously the simplest theoretical relation between s orbital spin density and nuclear geometry, which is based on perfect orbital following, should never be used. Although a good quantum mechanical calculation should give the correct relation, optimization of overlap is much cheaper and, judging by Table I, equally effective. The relation between  $\theta$  and  $\delta$ , as determined by overlap maximization, varies from molecule to molecule.<sup>27</sup> This suggests caution in applying the relation determined for methyl by Schrader and Karplus to other molecules.<sup>1a</sup> Special care should be taken when strongly polar bonds are involved.<sup>14</sup>

In retrospect it is obvious why aryl radicals have their half vacancy in the  $\sigma$  rather than in the  $\pi$  orbital.<sup>28</sup> Bond bending converts the competition for an electron between a localized sp<sup>2</sup> and a delocalized p orbital into one between a localized p (see % s in Table I) and a delocalized p. Analogous bond bending should be even more important in aryl cations, because of the importance of valence state promotion energy.

Bent bonds are reasonable for the pyramidal methyl radical, since it is planar in its lowest energy geometry, and the Hellman–Feynman force theorem predicts that such electronic distortion must accompany a deformation.<sup>29</sup> By the same token it is difficult to see how unconstrained radicals and carbenes can have bent bonds in their lowest energy geometries.<sup>30</sup> The “substituent antagonism” suggested by Bingham and Dewar seems reasonable for *tert*-butyl,<sup>31</sup> but the bond distortion in vinyl and methylene remains a puzzle.

**Acknowledgments.** This work was supported by the National Science Foundation (DMR76-01996) and by a Teacher-Scholar Grant from the Camille and Henry Dreyfus Foundation. I am grateful to Professors O. Sinanoglu, E. Wasserman, K. B. Wilberg, and D. E. Wood and particularly to Dr. M. D. Newton for helpful discussions.

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Received February 15, 1977

## A Novel Synthesis of 1,2-*cis*-Disaccharides<sup>1</sup>

Sir:

Much effort is currently devoted to the efficient and stereocontrolled preparation of 1,2-*cis*-disaccharides.<sup>2</sup> The availability of a general procedure is of paramount importance as it opens the way to many biologically and clinically active substances like antibiotics and antigens. As the scope for improvement of existing methods appears to be limited, novel reactions are desirable. The discovery in our laboratory that secondary amides react smoothly with halogeno sugars in the presence of a silver salt to give a new class of imidates paved the way to a novel method of selective activation of the anomeric center of carbohydrates, which appears full of promise in the field of glycosidic synthesis as amply demonstrated herein through the practical approach to eleven disaccharides.

A benzene solution of 2,3,4,6-tetra-*O*-benzyl- $\alpha$ -D-glucopyranosyl chloride<sup>3</sup> (1 equiv) was stirred for 12 h at room temperature in the presence of *N*-methylacetamide (1 equiv), silver oxide (3 equiv), diisopropylethylamine, and powdered 4-Å molecular sieves to give 1-*O*-(*N*-methyl)acetimidyl-2,3,4,6-tetra-*O*-benzyl- $\beta$ -D-glucopyranose (**1**, 88%) as a syrup,  $[\alpha]_{20}^{20} + 28.6^\circ$  (*c* 1.51, CHCl<sub>3</sub>).<sup>5</sup> The stereospecificity of this attack may be attributed to a push-pull mechanism at the surface of the insoluble silver oxide. This reaction is general and a variety of benzylated imidates have been prepared.<sup>6</sup> They all react with alcohols in various solvents and in the presence of *p*-toluenesulfonic acid to give a good yield of  $\alpha$ -glucosides.<sup>7</sup> A study of this glucosylation reaction using various imidates has shown that **1** is the best suited for this purpose.

In a typical procedure, methyl 2,3,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside<sup>8</sup> (**2**) was chosen as a crucial model for glucosylation at the redoubtable<sup>9</sup> 4-hydroxyl group of a hexopyranoside derivative (<sup>4</sup>C<sub>1</sub> chair form). A solution of aglycon **2** (0.5 mmol) in dry benzene (20 mL) was treated at room temperature with the imidate **1** (0.75 mmol) and *p*-toluenesulfonic acid (0.5 mmol) under rigorously anhydrous conditions. The solution was stirred for 6 days and neutralized with triethylamine. After workup and purification (silica gel column), methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- $\alpha$ -D-glucopyranosyl)- $\alpha$ -D-glucopyranoside was isolated as a clear syrup (3, 85%),  $[\alpha]_{20}^{20} + 48^\circ$  (*c* 1.05, CHCl<sub>3</sub>). After catalytic hydrogenolysis (Pd/C), methyl  $\alpha$ -maltoside was obtained as a foam (85%,  $[\alpha]_{20}^{20} + 172.5^\circ$ ).<sup>10</sup>

Similar glucosylation of methyl 2,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside<sup>8</sup> (20 h) followed by column chromatography gave the disaccharide derivative **4** as a colorless foam (81%); likewise, the isomaltoside **5** was obtained (80%), mp 101.5 °C  $[\alpha]_{20}^{20} + 59.3^\circ$  (*c* 1.78, CHCl<sub>3</sub>).<sup>11</sup>

The 2-hydroxyl group of D-galactopyranosides has been glucosylated in poor yield (25%) using either 2,3,4,6-tetra-*O*-benzyl- $\alpha$ -D-glucopyranosyl chloride<sup>2b</sup> or 2,3,4,6-tetra-*O*-benzyl- $\alpha$ -D-glucopyranosyl bromide<sup>12</sup> under halide ion cata-

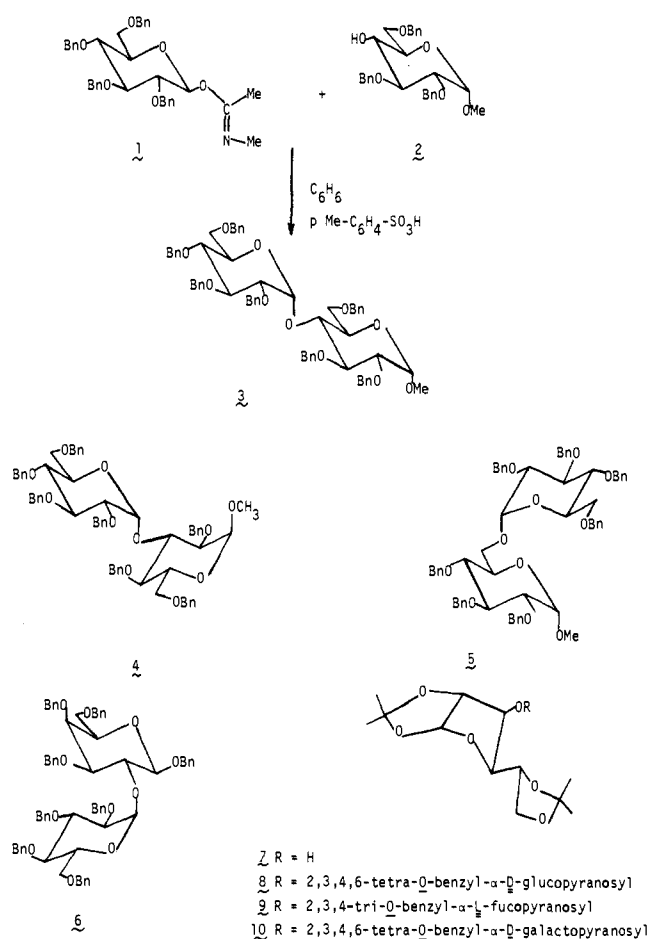


Table I.  $\alpha$ -L-Fucosylation of Various Alcohols Using the Imidate Derivative **13**

Alcohol	Protected disaccharide (or trisaccharide)	Yield, <sup>a</sup> %	Mp °C	$[\alpha]_{20}^{20}$ , <sup>b</sup> degree
<b>2</b>	<b>16</b>	74		-65.5
<b>7</b>	<b>9</b>	92	116-117	-118
<b>14</b>	<b>17</b>	84	129-130	+3
<b>15</b>	<b>18</b>	93	87-88	+2
<b>19</b>	<b>20</b>	86		+19

<sup>a</sup> No evidence for the formation of  $\beta$  anomer was obtained in any of the experiments. <sup>b</sup> In chloroform, *c* 1.

lyzed conditions.<sup>2c</sup> When benzyl 3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranoside<sup>13</sup> was glucosylated with **1**, the disaccharide derivative **6** was obtained (90%) as a pure foam,  $[\alpha]_{20}^{20} + 23^\circ$  (*c* 1, CHCl<sub>3</sub>). A further example of effective  $\alpha$ -glucosylation was provided by the reaction of **1** with 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucopyranose (**7**), where the protected disaccharide **8** was obtained in crystalline form (70%), mp 90-91 °C,  $[\alpha]_{20}^{20} + 46^\circ$  (*c* 2, CHCl<sub>3</sub>). A small amount of crystalline  $\beta$  anomer (3%) was isolated, mp 118-119 °C,  $[\alpha]_{20}^{20} + 1^\circ$  (*c* 1, CHCl<sub>3</sub>).

This imidate procedure was then applied to stereospecific  $\alpha$ -L-fucosylations, as  $\alpha$ -L-fucose containing oligosaccharides are of widespread occurrence in living systems. Under the agency of the Vilsmeier reagent,<sup>4</sup> 2,3,4-tri-*O*-benzyl- $\alpha$ -L-fucopyranoside<sup>14</sup> (**11**) was conveniently transformed into crystalline 2,3,4-tri-*O*-benzyl- $\alpha$ -L-fucopyranosyl chloride (**12**, 92%), mp 72-73 °C,  $[\alpha]_{20}^{20} - 169^\circ$  (*c* 1, CH<sub>2</sub>Cl<sub>2</sub>), which was in turn converted into 1-*O*-(*N*-methyl)acetimidyl-2,3,4-tri-*O*-benzyl- $\beta$ -L-fucopyranoside (**13**, 90%), mp 89-90 °C,  $[\alpha]_{20}^{20} - 67^\circ$  (*c* 1, C<sub>6</sub>H<sub>6</sub>). The imidate **13** has been most successfully used for the preparation of various protected di- and trisaccharides, as shown in Table I. Owing to its crystallinity, its